

# PLATINOTYPE,

BY

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## PREFACE.

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THE growing popularity of the Platinotype process has induced the Council of the Photographic Society of Great Britain to authorize a reprint of the translation of the brochure by Captain Pizzighelli and Baron Hubl, which appeared in the *Photographic Journal* in 1883. My friend and special colleague, the late Mr. J. F. Iselin, who made the bulk of the translation, and left me but small labour in editing it, has, alas ! passed away before the work reached its present stage. Had I now the benefit of his great linguistic knowledge, perhaps some slight modifications in the text might have been introduced ; as it is, I have left it nearly in the same state as that to which we both agreed three years ago.

W. DE W. ABNEY

May 1, 1886.

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# PLATINOTYPE.

## INTRODUCTION.

At the meeting of the British Association at Oxford, in 1832, Sir John Herschel<sup>1</sup> gave an account of some remarkable experiments on the action of light upon a salt of platinum. He prepared a solution of platinum in aqua regia, and neutralized it with lime; after carefully filtering this solution, he placed it in the dark and added limewater to it. At first no change took place; but after the lapse of some time a light flocculent precipitate was formed, no further reaction being observed so long as the solution remained in the dark. On such a solution, however (either the same which had been kept in the dark with the precipitate removed, or one freshly prepared in the same way as above), being exposed to sunlight it became at once clouded, and a white—or, with an excess of platinum, a yellow—precipitate was thrown down. The same reaction will occur, but less rapidly, on exposure to diffused light.

This precipitate was considered by Herschel to be a platino-calcic oxide; but according to Döbereiner<sup>2</sup> it consists of platinic chloride, platinic oxide, and lime. Judging from Johannsen's experiments,<sup>3</sup> however, Herschel's view seems to be the more correct: a solution of soda and baryta-water were found by Johannsen to behave in this reaction in the same way as lime.

Herschel observed that the platino-calcic solution is only affected by the violet end of the spectrum; when exposed to the light for days behind screens of liquids coloured yellow (solution of potassium bichromate) or red (tincture of rose-leaves with sulphuric acid), no alteration was observed.

According to Hunt (1844) a piece of paper dipped in a

<sup>1</sup> R. Hunt—"Researches on Light," 2nd edition, 1854, p. 152.

<sup>2</sup> Landgrebe—"On Light," 1834, p. 95.

<sup>3</sup> "Annalen der Chemie und Pharmacie," vol. 55, p. 204.



solution of platino-cyanide of potassium,<sup>1</sup> and hung up in the sun, undergoes a scarcely perceptible change even after a long exposure; but if the paper, after only a short exposure, is treated with mercurous nitrate, a weak positive image is produced, which can be fixed by means of a hot and dilute solution of carbonate of soda. Instead of a solution of mercury, one of nitrate of silver may be used equally well for developing the image.

The platino-cyanide of potassium paper, treated before exposure with the solution of mercurous nitrate, turns of a yellowish-brown colour, which in the light often becomes a beautiful scarlet-red; by a longer exposure this colour will be paler, and by continued exposure finally a weak reddish-brown. So that according as the duration of the action of light is greater or less, either a negative or a positive image will be the result.

Hunt observed that all the pictures prepared in this way are liable to fade; and it may happen that after some years such pictures will become inverted, so that what was originally a negative is converted into a positive.<sup>2</sup> The action of single parts of the spectrum on platino-cyanide of potassium paper appears to take place simultaneously in the extreme yellow and in the blue. In the more refrangible rays the action extends from the beginning of the blue well into the violet, but does not seem to overstep the visible spectrum. In the yellow the action is shown at first by the paper turning of a darker colour, but later on a gradual fading is observed.

Paper prepared with solutions of platino-cyanide of potassium and nitrate of silver becomes a deep violet colour under the action of light; and if a little mercuric chloride is added the colour will be developed by ammonia to a deep black. By dipping the developed image in a solution of mercuric chloride, the positive will be converted into a negative.

All these phenomena point, in our opinion, to the fact that by the exposure of platino-cyanide of potassium a reduction is effected, and that the compound thus produced possesses

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<sup>1</sup> Prepared by mixing a solution of platinic chloride with one of potassium cyanide.

<sup>2</sup> This change was noticed by Hunt in the case of pictures which had been kept for ten years in a portfolio.

the property of reducing the salts of silver and mercury. This explains the possibility of developing such pictures by means of these salts, since on those parts which have been affected by the light metallic silver or mercury, as the case may be, will be deposited.

Reasoning in the same way, we are also able to explain why paper containing mercuric chloride, in addition to the salt of platinum, will blacken on being treated with ammonia after exposure; the mercuric-chloride is reduced to mercurous-chloride. Similarly may be explained the observation of Hunt, that platinum pictures which had been kept in a portfolio in contact with silver paper were completely transferred to the latter; the parts which had been affected by light disappeared from the platinum paper, but were reproduced on the silver paper.<sup>1</sup> This remarkable fact induced Hunt to believe that it might be possible to employ the non-permanent platinum images for the production of pictures on other kinds of photographic paper. But this non-permanence, on which Hunt lays so much stress, may partly be due to the fact that these images are not really platinum, but more probably consist of imperfectly-fixed mercury or silver.

A solution of platinic-chloride in ether when exposed to the light, according to Gehlen,<sup>2</sup> first turns a straw-yellow colour, and then the reduced platinum separates in the form of a thin film on the sides of the glass vessel containing the solution. The same reduction process was observed by Döbereiner<sup>3</sup> in the case of mixtures of chloride of platinum with solutions of sodium tartrate, tartaric acid, formic acid, and oxalic acid, and also of chloro-platinite of potassium with potassic hydrate and alcohol. Hunt found that the same thing took place, if paper dipped in any of the above mixtures is dried and then exposed to the light. In these cases he observed that the parts which had been affected by light sometimes grew lighter and sometimes darker; and he was able to make the action visible, when the exposure had been short, by treating the image with a solution of mercurous nitrate.

<sup>1</sup> For similar observations of the transfer of photographs by contact, see Dr. Eder's "Manual of Photography," 1st part, p. 33.

<sup>2</sup> Landgrebe—"On Light," 1834, p. 92.

<sup>3</sup> Schweigger's "Year Book," vol. 17, p. 122.



Platinic iodide and bromide, which are both closely related to the chloride, behave, according to Hunt and Herschel,<sup>1</sup> in exactly the same way. Herschel found that images obtained with the iodide fade away, and the paper recovers its previous copying power; the same is true, according to Hunt, for platinic bromide. The latter observer remarked also that the alteration produced by the action of light is a very uncertain one, in that the affected parts sometimes became lighter, sometimes darker. According to Hunt, a mixture of platinic chloride and potassium ferricyanide is also sensitive to light, and gives blue images on paper through decomposition of the latter salt.

Starting with the above historical data, we have made it our task to investigate very carefully and closely the preparation of pictures by photography with the salts of platinum. By our researches we hope to have brought within the reach both of the amateur and the professional photographer a process of reproduction which, in our opinion, as regards the permanence as well as the artistic effect of the results, is a most important one.

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<sup>1</sup> Hunt—"Researches on Light," 2nd edition, 1854, p. 154.



# I.—THE THEORY OF THE PROCESS.

## *Preliminary.*

IN the presence of organic substances we find that the action of light causes in every case a reduction of the platinum salt ; that is to say, the salt corresponding to the higher oxide (platinic chloride or bromide) is reduced to that corresponding to the lower oxide (platinous chloride or bromide), and by still further exposure metallic platinum is separated. If, for example, a piece of paper dipped in solution of platinic chloride is exposed to the light, it will at first begin to fade in colour ; this is owing to the dark-coloured platinic salt being converted into the light pink coloured platinous salt ; and if the exposure is continued, the parts affected by the light will become black, owing to the separation of metallic platinum. The more easily oxidizable is the organic substance employed, the quicker will this reduction process be accomplished ; for instance, in the presence of oxalic or formic acid the blackening will take place much sooner than if the cellulose of the fibres of the paper alone be used. This reduction seems to explain the difference in the results obtained, as already mentioned, by Hunt in his experiments.

When the platinous salts are used, of course there will be no fading at first, but the exposed parts will at once turn black from the direct reduction of the salt to metallic platinum. It appears, however, certain to us that, previous to any blackening becoming visible—that is to say, with a short exposure of from ten to fifteen minutes in shadow—some change must have occurred in the platinous salt, since the parts that have been acted on by light have acquired the property of being more readily reduced by organic ferrous salts than would have been the case in their unexposed condition. An experiment of ours, which we made in the following way, illustrates this.

A sheet of paper was dipped in a solution of chloro-platinite

of potassium and oxalic acid, placed underneath a paper scale, and exposed to the light for fifteen minutes in a shady place. The paper, on which not the slightest effect of light could be seen, was then treated with a cold solution of ferrous oxalate and oxalate of potassium in water, so dilute as not to be capable of affecting in the slightest degree non-exposed chloroplatinite of potassium, and at once a well-defined image of the paper scale made its appearance. To what this change is due we were unable to determine; but the phenomenon reminds one of an analogous reaction in the case of slightly exposed silver chloride, in which the invisible image can be made to appear by means of the proper reducing agents.

In this respect the observation of Gehlen<sup>1</sup> is very remarkable, that a solution of platinic chloride in ether, after being exposed to the light, will be decomposed by ferrous sulphate, metallic platinum being separated. Gehlen supposes the cause of this change to be, either that platinic chloride suffers some alteration by the action of light, and is then more readily and completely reduced by the ferrous sulphate, or that the ether in the solution also produces an effect. It is well known that neither platinic nor platinous chloride alone can be precipitated by ferrous sulphate, but that when they are accompanied by some of the more readily oxidizable organic compounds (for instance, organic acids) the decomposition at once takes place. Now, as exposure of the ether solution of platinum induces the reduction of the platinic to the corresponding platinous salt, and therefore also promotes the formation of organic acids, it is possible that both the reactions given by Gehlen as the cause of the decomposition of the salt may come into play.

The question can, however, be solved indirectly by producing, by means of some sensitive substance, what may be called a provisional image, and then by an effective method converting this into one of platinum. The sensitive substance must, in the first place, answer the conditions on the one hand of being capable of being so altered by light as to acquire the property of reducing, under further treatment, the salts of platinum to the metal itself, and, on the other hand, of not possessing this property previous to exposure to the light.

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<sup>1</sup> Landgrebe—"On Light," 1834, p. 93.



Further conditions required by this substance are a sufficiently high sensitiveness to light, and the power of showing distinctly the alteration induced by the action of light; in other words, the provisional image must make its appearance quickly and clearly.

Of all the better known sensitive substances the salts of the heavy metals, for instance, those of silver, uranium, and iron, seem to be more especially well adapted to this purpose. These salts in the presence of organic substances undergo complete or partial reduction on exposure to the light, and in this state they possess the power of reducing salts of the precious metals.

# THE INDIRECT PRODUCTION OF THE PLATINUM IMAGE BY MEANS OF THE SALTS OF SILVER AND URANIUM.

1. *By means of Silver Salts.*—This process, which is occasionally practised, consists in treating with solutions of platinum a silver print obtained in the ordinary way, whereby (just as in toning with a salt of gold) platinum is partially or, with a longer continuation of the action, completely substituted for silver. So far as we know, Caranza<sup>1</sup> was one of the first to publish a definite method of toning silver prints with platinum; he used for the purpose a very dilute solution of platinum chloride in water, (1 : 2,000), acidulated with hydrochloric acid. This method is exactly like those afterwards recommended by Haackmann,<sup>2</sup> Watt,<sup>3</sup> Gwenthlian,<sup>4</sup> Sellon,<sup>5</sup> Maugham,<sup>6</sup> Kay,<sup>7</sup> and others.

Haackmann observed that prints on dull paper could be much more readily toned than those on albumenized paper; also that generally platinum baths are not so powerful as gold baths. Watt found that platinum prints produced in this way

<sup>1</sup> "Lumière," Feb., 1856, and "Photo. News," vol. I, 1859, p. 251.

<sup>2</sup> "Photo. News," vol. I, 1859, p. 251.

<sup>3</sup> *Ibid.*, vol. 2, 1859, p. 204.

<sup>4</sup> *Ibid.*, vol. 2, 1859, p. 263.

<sup>5</sup> *Ibid.*, vol. 8, 1864, p. 182.

<sup>6</sup> *Ibid.*, vol. 8, 1864, p. 184.

<sup>7</sup> *Ibid.*, vol. 14, 1870, p. 26.



were not liable to fade, although exposed to the light continuously for several years. According to Gwenthlian, acid solutions of platinum give black tones; alkaline solutions, brown ones.

Platinum toning-baths for paper prints have not, up to the present, met with general acceptance, in competition with those of gold, partly because the former are less active, and partly because the tones obtained by means of the platinum baths are inferior in point of variety to those obtained by the aid of gold. The reason why the platinum works less energetically than the gold bath is doubtless due to the fact that platinum salts are not so readily reduced as those of gold.

These platinum prints produced by means of silver images have been used in encaustic photography on glass and porcelain. In applying this process, Grüne<sup>1</sup> first converted a silver image on collodion into one of platinum, and then transferred the latter to the glass or porcelain, afterwards fixing it with a flux containing lead.

The method of intensifying negatives by means of salts of platinum is in principle analogous to that of toning paper prints. In this case the action of the platinum on the silver image is clearly of a chemical character, inasmuch as silver chloride is formed and metallic platinum is separated. For this reason intensification with platinum cannot, like that with pyrogallol or iron, nor like that with gallic acid in the gelatine emulsion process, be carried on to any desired extent, but has very definite limits.

Eder and Tóth<sup>2</sup> made some searching experiments on the action of platinic chloride on negatives produced by the wet process and developed with iron, and compared the action of platinum solutions acidulated up to different points and of different degrees of concentration. The best standard of dilution (although, according to their experience, much does not depend on the point) they found to be 1 part of platinic chloride in from 800 to 1,000 parts of water. More concentrated solutions act more quickly, whilst more dilute act less rapidly; but, if the action be continued for the proper length of time, the final result will always be the same. Hydro-

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<sup>1</sup> "Photo. Archiv," vol. 11, 1870, p. 230.

<sup>2</sup> "Photo. Correspondenz," vol. 12, 1875, p. 237.

chloric, nitric, or acetic acids added to the platinum bath<sup>1</sup> produced about the same effect: the silver image becomes black more rapidly,<sup>2</sup> but only by reflected light; by transmitted light it can scarcely be distinguished from the non-intensified negative. Neutral baths, according to these authors, give no advantage; they only work more slowly than acid baths.

To increase the density of the negative, Eder and Tóth converted the silver chloride which forms during the action of the platinum chloride into metallic silver, by flowing over the intensified negative, but without washing, a solution of ferrous sulphate (the iron developer); and they repeated the operation of platinizing and developing several times, as often as might be necessary. They found, however, that this process can only be repeated a limited number of times, since at the third or fourth repetition the platinum black will no longer adhere, and is washed away.

Eder and Tóth also tried whether the same reduction and precipitation as above described could not be effected by adding directly 20 grammes of ferrous sulphate to 500 cubic centimetres of the platinum solution acidulated with acetic acid; they found the result to be very much the same as if the platinum and iron solutions had been employed separately. This modification of the intensifying process, however, was not recommended by the experimenters, for the reason that a solution of platinum, containing ferrous sulphate, after standing some weeks, decomposes with the separation of metallic platinum. In the wet process intensifying with platinum alone will not, as a rule, give sufficient density, unless some other method be also employed; for this reason platinum as an intensifier is not much resorted to in practice.

Very recently Willis<sup>3</sup> has adopted the plan of intensifying gelatine-emulsion plates with platinum. For this end he converts a dark silver image into a white one of silver oxalate by treating it with ferric oxalate; he then washes it with

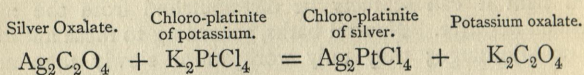
<sup>1</sup> To every 500 cubic centimetres of the solution of platinum chloride (1 : 800) were added 20 drops of nitric, or 30 drops of glacial acetic, or 20 drops of hydrochloric acid.

<sup>2</sup> The bath in which nitric acid is used works quickest; that acidulated with acetic acid is the slowest.

<sup>3</sup> "Photo. News," vol. 26, 1882, p. 183.



distilled or rain water, and flows over it a dilute solution of chloro-platinite of potassium. The latter salt decomposes the silver oxalate, forming chloro-platinite of silver :—



Now when this chloro-platinite of silver image is treated with the ferrous-oxalate developer, the whole of the silver, together with a portion of the platinum, is reduced to the metallic state.

The value of this intensifying process is, however, much affected by the property which the platinum salts have of rendering gelatine completely insoluble and impermeable, thus causing irregularities in the course of the intensification. Owing to this defect, the employment of platinum intensification for gelatine plates appears scarcely to be reliable.

Willis further found that the density of a gelatine negative can be increased by means of the ferric oxalate alone, without using any platinum salt. He submitted a negative to the action of ferric oxalate until it had turned quite white, washed it for two or three minutes in water, and then treated it with the ferrous-oxalate developer, which reduces the silver oxalate again to metallic silver. By this means he produced a greater density of the dark parts (which occasionally turn brown), and obtained the additional advantage that he avoids altogether any chance of the negative becoming tinted yellow, as happens when the pyrogallic developer is used. How Willis really attains a denser negative by thus working in a circle, as it were, is not clear to us ; unless, indeed, that by the basic salts of iron depositing on the parts affected by the light, the density of those parts is increased.

2. *By means of Uranium Salts.*—Of the indirect production of platinum images by means of the salts of uranium we have been able to find only very meagre notices in photographic works and journals. According to Van Monkhoven,<sup>1</sup> Niépce de St. Victor was the first to make any attempts in this direction ; he exposed a sheet of paper dipped in uranium nitrate to the light, and developed the scarcely visible image which

<sup>1</sup> "Bull. de l'Assoc. Belge de Phot.," vol. 6, p. 335.



was formed of the uranous salt, by treating it with a solution of gold or platinum. Bollmann<sup>1</sup> also employed the salts of platinum for the production of uranium images; he did this in two ways:—1st, by applying a mixture of the uranium salt and the platinum salt directly to paper, afterwards intensifying with a solution of some other metal, such as gold; 2nd (which is also Krone's<sup>2</sup> method), by converting the uranium into a silver image, and then into one of platinum.

None of these processes have been adopted in general practice. The defect which qualifies every urano-platinum process is that the image obtained after exposure is almost invisible, as the action of light produces only a slight change of colour from light yellow to light green; hence the time necessary for exposure could only be estimated by using a properly arranged photometer. From our own experiments we are of opinion that the process can be carried out much in the same way as the platino-ferric process which will be found described further on. But we believe that the above difficulty of copying on uranium paper, added to the high price of the uranium salts, will render the adoption of this process impossible in practice.

#### THE INDIRECT PRODUCTION OF THE PLATINUM IMAGE BY MEANS OF THE SALTS OF IRON.

THE facility with which the organic salts of iron can be reduced by light is capable of manifold application in photography. Both Hunt and Herschel<sup>3</sup> were aware of the reaction, and took advantage of it in their photographic experiments. They used paper dipped in solutions of ferric citrate or oxalate, or of the double salts of ammonium, and having exposed it to the action of light, they converted the ferrous image thus obtained into one of gold, silver, mercury, or prussian blue, by developing with solutions of gold, silver, mercury, or ferricyanide of potassium, as the case might be.

<sup>1</sup> Bollmann's "Phot. Monatshefte," 1862, p. 37.

<sup>2</sup> "Bulletin de la Soc. Française de Photo.," vol. 28, April, 1882.

<sup>3</sup> R. Hunt, "Researches on Light," 2nd edition, 1854, p. 163.

Van Monckhoven<sup>1</sup> repeated these experiments in 1863, and published directions for carrying out the process.

These experimenters do not appear to have tried the effect with the salts of platinum; at least, we can find no mention of any researches on the subject in their publications. As, however, the salts of platinum are readily reduced by the ferrous salts, the latter seem to be peculiarly fitted for the production of platinotypes. Hunt<sup>2</sup> believed that he could turn this reaction to advantage in photography by dipping paper in a mixed solution of ferric oxalate and platinic chloride, and when dry exposing it to the light. After an exposure of a few minutes he found that the part of the paper which had been acted on by light was considerably darker than the part which had been protected from the light; but when the exposure was continued for a longer time, he noticed that the dark parts faded again. His hopes of obtaining in this way more vigorous images than by applying the salts of platinum alone were therefore disappointed. But the true explanation of the phenomenon lies in the fact that the salts of platinum are only reducible by solutions of the ferrous oxalate formed during the exposure; the change in colour observed by Hunt must be attributed virtually to the salt of iron. It is true, as was stated in the Introduction, that the salt of platinum also undergoes a change of colour after an extended exposure; but this is so trifling in comparison with that of the ferrous oxalate that it is neglected in the observation.

Merget<sup>3</sup> also, in 1873, attempted to take photographs in platinum indirectly by means of the iron salts. He used in his experiments a solution of platinum chloride mixed with one of ferric-chloride and tartaric acid. Paper dipped in this mixture and exposed to the action of light under a negative gave a white image in ferrous chloride on a yellow ground. The deliquescent ferrous chloride absorbed moisture from the atmosphere, and in this state it was said, in conjunction with the simultaneous exhibition of mercurial vapour, to complete the reduction of the platinum. Pictures taken in this

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<sup>1</sup> "Bulletin Belge de la Photographie," vol. 2, 1863, p. 29.

<sup>2</sup> R. Hunt, "Researches on Light," 2nd edition, 1854, p. 157.

<sup>3</sup> "Photo. Correspondenz," 1873, vol. 10, p. 105.



way were then washed with weakly acidulated water, in order to remove the remaining salts of iron. Besides those of mercury, Merget also employed the vapours of hydrogen, sulphuretted hydrogen, and iodine. In his opinion, the conditions of success in working this method depend not only on the more or less appropriate choice of sensitive substances, but also on the proper preparation and physical properties of the sensitive films. When prints are produced by the direct or indirect reduction of the salts of the precious metals, the vigour of tone produced depends, according to Merget, materially on the grain of the sensitive film. This may be obtained by the happy selection of the proper kind of paper, or by the addition of certain substances which, though in a state of fine crystals or of powder, are yet insoluble, so that their particles nestle in between those of the sensitive substance. This process for the indirect production of the platinum image, as described by Merget, never seems to have got beyond the experimental stage; at least, we were unable to find in the literature of the subject any further account of it.

At all events, whenever the salts of platinum are used for the production of images in the same way as those obtained with the salts of gold and silver, more energetic reducing agents are required than in the case of these latter. For instance, the platinum will not be entirely precipitated from a solution of platinic chloride by means of ferrous oxalate alone; it can only be effected by increasing the reducing action by exhibiting at the same time potassium oxalate. In order, therefore, to convert an image obtained by the action of light on ferric-oxalate paper into one of platinum, it is necessary to have present, besides the salts of platinum, substances which, like the soluble oxalates, tartrates, citrates, &c., will increase the action of the ferrous salt. This seems to have been known to Willis, for he bases on it the platinum printing process called after his name.<sup>1</sup> This process, for which he took out a patent in England in 1873, is essentially as follows:—A solution of a salt of platinum, iridium, or gold, or also of a mixture of these salts, is applied to the surface of paper, wood, or some other suitable material, and

<sup>1</sup> Specification of W. Willis, jun., No. 2011, 5th June, 1873.



dried; it is then coated with ferric oxalate or tartrate, again dried, and exposed to the light under a negative. A faint brown image will appear, which, after being brushed over with a solution of potassium oxalate, turns a strong, intense black.

The following instructions were given by Willis:—

1. Coat a piece of paper with a solution of 1 part chloroplatinate of potassium in 48 parts of water. When it has been dried, dip the paper in a solution of 1 part nitrate of lead in 48 parts of water. Dry once more, and brush over with a solution of 1 part ferric oxalate in 8 parts of water, to which, in order to render the oxalate more soluble, a little oxalic acid has been added. After again drying, the paper must be exposed under a negative, and then put to float on a hot solution of potassium oxalate. Finally, it must be washed in a weak solution of oxalic acid in water, then in sodium hyposulphite, and lastly again in water.

2. Proceed as in the previous case, only substituting for the lead solution one of 1 part silver nitrate in 60 parts water. When the prints are taken up from the weak solution of oxalic acid, they must be dipped either in a strong solution of ammonium chloride or in a weak solution of the same salt, and then in a weak one of ammonia. Finally rinse well in water.

3. The paper is first dipped in a solution of 1 part platonic bromide in 40 parts water, then dried, then again dipped in a strong solution of ferric tartrate, and afterwards once more dried. It is now exposed beneath a negative, and the image thus obtained is developed by floating on a hot solution of potassium oxalate. Afterwards it is immersed in a weak solution of oxalic acid, finally rinsed in water, and dried.

For the platinum process described above, with which Willis, according to his own statement, produced excellent results, he substituted, in 1878, a modification, by means of which he was enabled to take, with more ease and security, prints showing much greater uniformity, and possessing a higher degree of permanence. This improvement was made the subject of a second patent,<sup>1</sup> according to which the prin-

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<sup>1</sup> Specification of W. Willis, jun., No. 2800, 12th July, 1878.

cial points were the entire elimination of the silver salt, and the addition to the developer of chloro-platinite of potassium. The following short extract from the specification will give an idea of the nature of the process :—

Paper, or some other suitable support, is dipped in a solution of

Water...	...	...	30	parts.
Chloro-platinite of potassium			1	"
Ferric oxalate	...	...	4.5	"
Lead chloride	...	...	0.13	"

Having been dried, the paper is then exposed beneath a negative, and the image is developed by floating on, or dipping in, a hot solution of

Water...	...	...	30	parts.
Potassium chloro-platinite	...	...	0.5	"
Potassium oxalate	...	...	8	"

The further manipulations remain precisely the same as in the previous process. In this specification Willis further states that, in place of the above-mentioned platinum salts, he can also use other salts of platinum, as well as the salts of other metals, such as gold, iridium, or palladium; also, that he is able to dispense altogether with the chloride of lead, or can substitute for it chloride of mercury; lastly, that he can add to the developer other salts of platinum or the salts of other metals instead of the chloro-platinite of potassium, but that in general he prefers the latter.

In 1880 Willis took out a third patent<sup>1</sup> for a still further improvement of the platinum process; in this he proposed to increase materially the amount of platinum salt in the sensitizing bath, but, on the other hand, to omit the use of silver or lead salt, and in the developing bath that of platinum salt. By this arrangement, not only is the process much simplified, and the expense reduced, but also any fear of discolouring the white parts of the image—which so often happens when lead or silver salts are employed—is altogether avoided.

<sup>1</sup> Specification of W. Willis, jun., No. 1117, 15th March, 1880.



Willis, according to this specification, gives the following instructions for preparing the sensitizing bath :—<sup>1</sup>

Water ... ..	30	parts.
Potassium chloro-platinite ...	4'2	„
Ferric oxalate... ..	4'2	„

and he further mentions that in this improved process he applies a minimum of 0'12 gramme, generally, however, 0'27 gramme, and even more of potassium chloro-platinite per 1,000 square centimetres of surface. He also speaks of improved developing-solutions which may contain the citrate or tartrate of sodium, potassium, or ammonium, or mixtures of these salts, as well as the acetates of the above-named metals, and the mono- or diphosphate of ammonium or the mono-phosphate of sodium. Of the properties and action of these developing solutions nothing is said in the specification : the salts are merely enumerated.

Since the above-named dates several attempts have been made to imitate or modify this process for taking platinotypes, but without satisfactory results. For instance, Dr. Koninck published<sup>2</sup> a process very much like the one of Willis, only using platinum chloride instead of platinous chloride. Dr. Koninck, however, only succeeded in obtaining a grey tone in his pictures ; and this is due to the circumstance that chloride of platinum is generally very acid, which would prevent the reduction from being thoroughly carried out. That this is the true cause of the defect is shown by Koninck's further observation, that, by employing a solution of Rochelle salt, rendered alkaline with caustic soda, he was able to obtain better results.

By a similar method Roppe,<sup>3</sup> in 1880, in order to render Willis's platinum process more capable of general application in practice, suggested the substitution of platinic chloride or of the double salt of platinum and sodium (both of which are readily obtainable) for the less known potassium chloro-

<sup>1</sup> In this specification, Willis lays stress on the fact that he proposes to use the *platinous* salts, whereas in his previous specifications he mentions only *potassic chloro-platinite*.

<sup>2</sup> "Photographische Mittheilungen," vol. 16, p. 73.

<sup>3</sup> "Bulletin de l'Association Belge de la Photographie," vol. 6, p. 302.

platinite. He also proposed to add this latter salt to the developer, the same as Willis does in his second process. This method, however, possesses the great disadvantage that the ferrous salt formed in the developing bath, especially when the latter is deficient in platinum, is dissolved out before it has had time to effect the necessary work of reduction, and it therefore becomes difficult to make the prints sufficiently vigorous. On the other hand, it must be recollected that in operations with a developer containing platinum considerable loss is inevitable through splashing, adhesion of the solution to the prints, &c., so that the process becomes too expensive for working in general practice.

Both these defects are satisfactorily got rid of by Willis, in his latest improvements, by using no platinum in the developer, but, in its place, adding a larger quantity of the metal to the sensitizing bath. In this way the exposure to light brings out a provisional image in ferrous oxalate, which, on dipping into the developing-liquid, is converted into one of platinum, just as if a platinum bath had been formed in the film itself.

We have been induced by the many and great advantages offered by the platinum process, by its remarkable sensitiveness, by the simplicity of the manipulations required, by the permanence of the prints, and by the facility with which effects scarcely obtainable in any other way can be produced, to devote special attention to this process. Since, however, in Willis's specifications of patent, for causes which can be readily understood, only general instructions are to be found, and no reason is given for the selection of any particular preparation, as also the account of the results obtained by use of the substances specified is altogether wanting, we found ourselves compelled, quite independently of these publications, to undertake a series of investigations of all the salts of platinum and iron which, in our opinion, could be used for photographic purposes, as well as to study closely the capabilities of different developing-solutions.

#### THE SALTS OF IRON.

All the ferric salts are, in the presence of organic bodies, more or less sensitive to light, the ferric salts being by the action of light reduced to the corresponding ferrous salts.



In principle, therefore, every ferric salt is capable of being used for the production of platinum images, so long as some organic substances, such as paper, gelatine, or starch, is employed as a support for the image. Those salts, however, must have the preference by whose aid the reduction is accomplished in the least possible time,—that is to say, those which permit of the exposure to light being reduced to a minimum. In selecting the particular salt of iron care must also be taken that in the operation of reduction none of the stronger acids, especially the mineral acids, are set free, as they are antagonistic to the reduction of the platinum salt, and so prevent the development of the image. For this reason the so highly sensitive mixture of ferric chloride and oxalic acid cannot be employed, since under exposure free hydrochloric acid is developed. It will be found that the compounds of ferric oxide with the organic acids,—in other words, the organic ferric salts,—are best adapted to secure the fulfilment of the above-named conditions.

Of all these salts, according to the researches of Dr. Eder,<sup>1</sup> the oxalate and its double salts take the first rank as regards sensitiveness to light; and then follow the tartrate and the citrate. Dr. Eder determined the sensitiveness of the aqueous solutions of these ferric salts from the amount of ferrous salt precipitated by the action of light in the same time. The following is his table of the results of the photo-chemical decomposition of the ferric salts obtained in this way, at a temperature of from 17° to 20° C.:—

Ferric chloride + oxalic acid	...	...	100
Ferric oxalate	...	...	89
Ammonio-ferric oxalate	...	...	80
Potasso-ferric oxalate	...	...	78
Ferric tartrate	...	...	80
Ammonio-ferric tartrate	...	...	80
Ammonio-ferric citrate	...	...	15
Ferric chloride + citric acid	...	...	19
Ferric chloride + tartaric acid	...	...	25

<sup>1</sup> Dr. Eder, "Recent Investigations on the Sensitiveness of the Salts of Iron," "Photo. Correspondenz," vol. 17, p. 219.

The numbers here given are only correct when the solutions contain from one to five per cent. of ferric chloride, or the equivalent amount of ferric salt. As a general rule, the sensitiveness increases with the degree of concentration, at the same time that the differences in the quantities of ferrous salt precipitated from the solution become smaller.

For this reason the mixtures of the above-mentioned ferric salts when dried into paper behave quite differently from the aqueous solutions when exposed to the light. In order to discover the variations in sensitiveness under these circumstances, Dr. Eder soaked strips of paper in the different solutions of the salts, and, when they were dry, exposed them simultaneously to the light under one of Vogel's paper photometers. By then treating these strips with a solution of ferricyanide of potassium he was able to read the degree of light-action by the depth of the blue colour brought out. In these experiments the same order was shown in the degrees of sensitiveness as in those with the solutions: the mixture of ferric chloride and oxalic acid proved to be the most sensitive of all; the ferric oxalate was less so; then follow the ammonio- and sodio-ferric oxalate, and the potasso-ferric oxalate was the least. The differences in sensitiveness between the double salts alone were not so great as in the case of the aqueous solutions, —the sodium and ammonium salts, especially, being almost equally sensitive.

Probably the reduction which these salts undergo under the influence of light is principally due to the fact that with the formation of the corresponding ferrous salt carbon is separated as carbonic acid. This decomposition of the aqueous solutions when exposed to the light was first observed by Döbereiner<sup>1</sup> in the year 1831; afterwards by Suckow,<sup>2</sup> Draper,<sup>3</sup> Reynolds,<sup>4</sup> and Eder.<sup>5</sup> The reaction is most regular in the case of the oxalate, as the quantity of carbonic acid given off agrees very closely with that determined theoretically; it is not so regular in the case of the citrate and the tartrate,

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<sup>1</sup> "Schweigger's Journal," vol. 62, p. 90.

<sup>2</sup> "On the Chemical Action of Light," 1832, p. 29.

<sup>3</sup> "Dingler's Polytechnic Journal," vol. 146, p. 29.

<sup>4</sup> "British Journal of Photography," 1861, p. 9.

<sup>5</sup> "Photo. Correspondenz," 1880, vol. 17, p. 219.



since, in addition to carbonic acid, acetic and oxalic acids are also formed.

Of all these salts of iron examined by Dr. Eder, the most sensitive, the mixture of ferric chloride and oxalic acid, cannot unfortunately be used in the production of platinum prints, as already mentioned above. On the other hand, it was expected that the oxalate, citrate, and tartrate would be more generally serviceable. To satisfy ourselves on this point we made the following experiments:—Solutions<sup>1</sup> of the salts in question were mixed with equal quantities of potassium chloro-platinite, and applied to the paper; strips of this paper were then dried and exposed to the sunlight, underneath a paper scale, for equal periods of time. When developed with a hot solution of potassium oxalate, it appeared that (1) the black colour on the strip prepared with ferric oxalate was much more intense, and (2) its sensitiveness considerably greater, than was the case with the strips prepared with the tartrate and citrate. Experiments with the acetate and the formiate proved that the former is very little sensitive, and that the latter causes the reduction of the platinum salt very rapidly, and even without exposure to light.

The double salts of the ferric oxalate possess the great advantage of being readily procurable in a crystalline form—a property altogether wanting in the ferric oxalate alone. It became, therefore, important to submit these salts to an examination in respect to their suitability for the platino-ferric process. The potassium salt cannot well be employed, on account of its insufficient solubility; but the sodium and ammonium salts, of whose composition, especially of the amount of water of crystallization contained in them, Dr. Eder's investigations have given complete information, are also unable to comply with the requirements. The paper prepared with these salts is only slightly sensitive, and the photographs taken thereon are inferior as regards intensity and depth in the shadows to those produced by the aid of ferric oxalate. This unsuccessful result may be explained on the supposition that the complete reduction of the double salts under exposure

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<sup>1</sup> The degree of concentration of the solutions was so arranged that, after exposure, there might be one molecule of platinous chloride to every two molecules of the ferrous salt.

is not effected with the same readiness and regularity as is the case with ferric oxalate. We endeavoured to rectify this by reducing the quantity of the double salt in the sensitizing solution by one-half, and making up the requisite amount of iron by the addition of neutral ferric chloride. But, even with this combination, we were unable to obtain reactions of any great value; though the intensity of the blacks was improved, the sensitiveness was still further lowered, and, besides, the prints had a nasty yellow-brownish tone.

Through the above-mentioned experiments we arrived at the conclusion that in platinum-printing only ferric oxalate can be employed with advantage; consequently, in our further experiments we considered this substance alone as the sensitizer. Ferric oxalate is produced by dissolving ferric hydrate in oxalic acid;<sup>1</sup> a greenish-brown solution is obtained, which, on being evaporated, leaves a brown syrup, not capable of being crystallized. When perfectly protected from the light, and at temperatures of from  $15^{\circ}$  to  $30^{\circ}$  C., this solution will keep for months without undergoing alteration.<sup>2</sup> At a higher temperature, however, as, for instance, when heated for several hours to  $50^{\circ}$  C., a gradual reduction to ferrous oxalate takes place; and this reduction will be effected much quicker if the solution, or paper coated with it, is exposed to the action of light. The ferrous oxalate thus formed consists of a light yellow crystalline powder, soluble with difficulty in water,<sup>3</sup> but which even in a moist condition resists the action of light and air.

Moistened with solutions of the alkaline oxalate, Dr. Eder found that this salt has a very powerful reducing action, and, according to our experience, solutions of the alkaline acetates, benzoates, succinates, borates, and phosphates, as well as the solutions of the alkalis and of the alkaline carbonates, produce the same effect. In this reaction are formed either soluble double salts or insoluble ferrous salts having energetic reducing effects; with the caustic alkalis, and especially with the alkaline carbonates, ferrous oxide itself is formed—a well-known reducing agent.

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<sup>1</sup> For the details of this process see further on, under "Practical Instructions."

<sup>2</sup> Dr. Eder and E. Valenta, "On the Iron Oxalates and some of their Double Salts," Transactions of the Imperial Academy of Science at Vienna, Part 2, October, 1880.

<sup>3</sup> One part of the salt dissolves in 1,000 parts of water at  $15^{\circ}$  C.

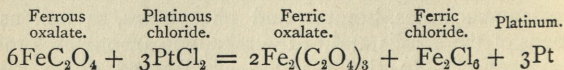


## THE SALTS OF PLATINUM.

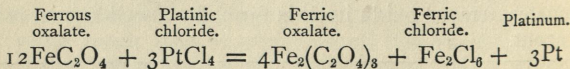
IN the process now before us, the salts of platinum play a much more important part than those of iron, as from them is derived the metal of which the image finally is composed. As already stated, in the production of this image the salts are reduced; hence only those salts of platinum are suitable which are capable of being readily reduced by the above-mentioned reducing agents, and which, for this purpose, require the use of comparatively small quantities of the ferrous salts. Further, as in sensitizing the paper the salt of platinum is applied simultaneously with that of iron, all those compounds of platinum are excluded from consideration which, in mixing with the salts of iron, may give rise to disturbing reactions. Of all the salts of platinum, the chloride, bromide, and iodide seem best to fulfil the first of these conditions; while the sulphite, the double cyanide compounds, and the double salts of ammonium and platinum are either not reduced at all, or are reduced with very great difficulty. Independently of this, however, the first-named salts are to be preferred, on the ground that they can be prepared more easily, and are therefore cheaper.

The chemical reaction in the formation of the image is, according to Berkeley,<sup>1</sup> most simply represented by the following equations:—

For platinous chloride—



Analogous is that for platinic chloride—



The correctness of these equations is, however, rendered

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<sup>1</sup> "Phot. News," 1882, p. 157.

doubtful by our observation of the formation of gas when the image is developed in a hot solution of potassic oxalate. Now, this reaction can only be due to the fact that the remainder of the oxalic acid combined with the iron is displaced by chlorine, and separates as carbonic acid in a gaseous form. We may therefore assume that the reaction is not quite so simple as the equations would indicate, but is probably much more complicated. It should also be borne in mind that the platinum salt itself, as we have already had occasion to mention, undergoes a slight alteration under exposure to the light.

But, whatever the real process of reduction may be, it is clear that the platinic chloride requires just twice as much ferrous oxalate for its complete reduction as the platinous chloride. This explains why it is scarcely a matter of no importance whether with Willis we employ, for developing the image, a platinous salt, or, with Koninck and Roppe, a platinic salt. The quantity of ferrous salt need not be so large in the first case as in the second; and as the ferrous oxalate is only formed by exposure, the duration of that exposure may be considerably less, when a platinous salt is used, than is required in the case of a platinic salt.

As in every other photographic printing process, we find also in this, that the more sensitive substance gives soft pictures with a hard negative, and with a soft negative weak pictures, while the substance requiring a longer exposure will give, in the one case, a hard, in the other a brilliant, picture. It will, therefore, be most advisable to employ generally a platinous salt as the sensitizer, and to mix with it, when the negative is soft, a little of the corresponding platinic salt, or, when the negative is weak, a larger quantity of the latter.

According to our own experience, of all the platinous salts, the platinous chloride and the double salts of platinous bromide best comply with all the required conditions, and, of the latter, the platinous bromide of potassium is to be preferred. The double salts of platinous iodide cannot be used, as in mixing with the ferric oxalate salt they reduce it, with separation of iodine. The corresponding simple salts—that is to say, the platinous chloride and bromide—are insoluble in water; before they can be used, therefore, they must be dissolved in solution of the corresponding haloid acids—a process



which, as has already been explained, cannot be carried out, on account of the free acid present.<sup>1</sup>

Potassium chloro-platinite and the corresponding bromo-platinite possess the advantage of being easily prepared and purified, but, on the other hand, the disadvantage that they cannot be mixed with platinic chloride and its double salts without the formation of an insoluble precipitate of potassium chloro-platinate. This defect is not found to exist in the case of the sodium, lithium, and magnesium double salts; but the two first crystallize only with difficulty, and it is on that account troublesome and costly to obtain them pure. Besides, they are hygroscopic and deliquescent in a high degree; and as the quantity of water they contain is so variable, they cannot be accurately weighed without special arrangements and precautions. The magnesium salt is not deliquescent; but it does not readily crystallize, and cannot, therefore, be easily obtained in a pure state. The calcium, barium, and strontium salts cannot be used, from the fact of their forming insoluble precipitates with ferric oxalate.

A consideration of the comparative advantages and disadvantages possessed by the above-mentioned platinum compounds led us to give the preference to the potassic salts; and, as the preparation of the potassium bromo-platinite is much more troublesome than that of the corresponding chloro-platinite, we determined to carry on our experiments with potassium chloro-platinite. We desire, however, to draw attention to the circumstance that, according to our experiments, the double salts of potassium, sodium, lithium, and magnesium all give identical results in the production of the image, both as regards their reducing powers and as regards the appearance of the finished picture.

When preparing a sensitizing solution of chloro-platinite of potassium, adapted to the character of the negative from which

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<sup>1</sup> True platinous chloride (the formula for which is  $\text{PtCl}_2$ ) is, like platinic chloride ( $\text{PtCl}_4$ ), insoluble in water. Dissolved in hydrochloric acid, it forms chloro-platinous acid ( $\text{PtCl}_2 \cdot 2\text{HCl}$ ), a substance which corresponds to chloro-platinic acid ( $\text{PtCl}_4 \cdot 2\text{HCl}$ ). The latter compound is generally, but incorrectly, designated platinic chloride; commercial platinic chloride contains, in addition, six molecules of water of crystallization. For the sake of brevity, we follow the common practice, and call the compound above alluded to ( $\text{PtCl}_4 \cdot 2\text{HCl} + 6\text{H}_2\text{O}$ ) platinic chloride.

the copy was to be taken, we were compelled to leave out of the question the direct addition of a platonic salt, partly because a mixture with the double salts of platonic chloride is not feasible, partly on account of the difficulty and expense of preparing a more suitable platonic salt. But we tried whether the required advantage could not be obtained by adding the oxidizing substances, which have not the effect of immediately decomposing the sensitizing solution, but only convert more or less of the platinous into the corresponding platonic salt at the time when the solution dries up on the support. This point we shall go into with more detail further on.

#### THE SUBSTANCES SUITABLE FOR THE DEVELOPMENT OF THE PLATINUM IMAGE.

When a sheet of paper, sensitized with a mixture of potassium chloro-platinate and ferric-oxalate is exposed to the light, a weak but perfectly visible image is formed, consisting principally of ferrous oxalate.<sup>1</sup> As the ferrous oxalate possesses some slight power of reduction, the treatment of the image with hot water will partially reduce the platinum salt. But this reduction will be more complete, that is, the image will appear more vigorously, if there be selected for the developing solutions substances which are able to increase the action of the ferrous oxalate. When treating of the salts of iron, we cursorily mentioned substances of this kind, and described their mode of action. Solutions of these substances we will, for the sake of brevity, call developers. Some of them act best when cold and in a dilute condition; others, on the contrary, must be used hot and in concentrated solutions, in order that the reduction may be carried out as quickly and perfectly as possible. If the reduction is slow, both the platinum and ferric salts might be dissolved before they had time to act on one another. The reaction would then either not be effected at all, inasmuch as the dilute solutions are

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<sup>1</sup> The alteration effected in the platinum salt is, with the very short exposure which is sufficient to produce the image, not appreciable by the eye.



unable to act on one another, or it would take place only in the developing liquid, and not on the support of the image.

The following developers have been tested by us, and are enumerated below in the order of their reducing power; and it must be here noted that, with the exception of the caustic alkalies, the carbonate of sodium, and the ammonia, they are all applied in a hot ( $80^{\circ}$  C.) and concentrated condition:—<sup>1</sup>

(1) *Sodium acetate* acts very energetically, and gives soft pictures, which, however, owing to the formation of basic ferric acetate, have a yellowish tinge. Although this yellow colour can be nearly entirely got rid of by subsequent treatment with hydrochloric acid, we endeavoured to prevent the separation of the insoluble ferric acetate by rather strongly acidulating the developing bath with oxalic or citric acid.

(2) *Sodium acetate + oxalic acid* works exactly the same as sodium acetate alone, but gives pure whites.

(3) *Potassium citrate* behaves almost identically with (2).

(4) <i>Sodium carbonate</i> in a hot solution ... ..	} All these act much the same; only those solutions numbered (4), (9), and (10) give, through the formation of basic ferric salts, yellow-coloured images. There also is formed in the developing bath (for the same reason) an insoluble precipitate.
(5) <i>Ammonium citrate</i> (neutral) ... ..	
(6) <i>Ammonium citrate</i> (acid, as used for developing chloride-of-silver pictures) ... ..	
(7) <i>Potassium oxalate</i> ... ..	
(8) <i>Rochelle salt</i> ... ..	
(9) <i>Ammonium benzoate</i> ... ..	} These act almost identically the same, but are considerably inferior developers to those before mentioned.
(10) <i>Sodium succinate</i> ... ..	
(11) <i>Caustic potash</i> (dilute solution, 1 : 25) ... ..	
(12) <i>Sodium carbonate</i> ... ..	
(13) <i>Sodium phosphate</i> ... ..	

<sup>1</sup> We carried out this experiment by cutting into strips a piece of platinum paper which had been exposed beneath a paper scale, and developing these strips in various solutions.

(14) <i>Water</i> (hot)	...	...	} Possess only a moderate power of developing.
(15) <i>Ammonia</i> ...	...	...	
(16) <i>Oxalic acid</i> ...	...	...	

In practically working the platinum process the citrates must be altogether left out of the question, as they are too expensive; sodium carbonate, ammonium benzoate, and sodium succinate are not adapted for the purpose, for reasons previously stated. Caustic potash, sodium phosphate, and the solutions numbered (14), (15), and (16) are equally useless, as they do not act sufficiently energetically.

We recommend the mixture of sodium acetate and oxalic acid, the potassium oxalate and the Rochelle salt, as the best developers; and of these three we give the preference to potassium oxalate, notwithstanding its somewhat higher price. This salt is now largely used in the negative process, and will therefore find a place in most laboratories, whether of amateur or of professional photographers.

#### THE EFFECT OF THE PRESENCE OF FOREIGN BODIES IN THE SENSITIZING AND IN THE DEVELOPING SOLUTION.

Many substances, when present in the developing or still more in the sensitizing solution, produce special effects on the composition and character of the image. To prevent mischief, therefore, the greatest care must be taken to secure perfect purity and exactly correct composition in the chemicals employed; also to attend conscientiously to the preparation of the solutions.

*Influence of Acids.*—Both the sensitizing and the developing solutions must have a distinctly acid reaction; when this is not the case, the paper will, owing to the formation of basic salts of iron, have a yellow colour which does not disappear after treatment with dilute hydrochloric acid, or even with a mixture of the latter and sulphuric acid. Ignorance of this fact was, at first, with us the cause of many failures; we can only strongly advise that particular attention should be paid to this point. In another respect an excess of acid acts just as injuriously as an insufficiency; this is true both for organic acids as well as (and in a higher degree) for free mineral acids.



Excess of acid in the sensitizing solution prevents complete reduction of the platinum, and hence is the cause of the picture being weak. The reason for this phenomenon is probably due to the circumstance that, in developing, potassium binoxalate forms in the print, which has but little power of dissolving ferrous oxalate. At the same time some of the very soluble platinum salt passes into the developing solution before it can be reduced in the image-film. Especially with an excess of oxalic acid<sup>1</sup> we observed the effects of solarization; the deepest shadows of the picture have then a grey instead of a black tone, and this grey is even lighter than the adjacent darker half-tones. Acid solutions also penetrate the paper more readily than neutral ones; a very acid sensitizing solution would, therefore, enter too deeply into the paper, and would even come through on the other side. In this way the image, instead of being on the upper surface, would be in the interior of the paper, and would lose all vigour.

After numerous attempts we came to the conclusion that mineral acids must absolutely be avoided,<sup>2</sup> and that (as previously remarked) the ferric oxalate solution must be acidulated with oxalic acid in the proportion of six to eight grammes of oxalic acid to every hundred grammes of the salt.

The presence of free acids exerts a peculiar effect on the colour-tone of the picture. When quite neutral<sup>3</sup> solutions are used, the picture assumes a brownish-black colour; but if they have a slightly acid reaction, it has a bluish tone. These effects remind us of the analogous phenomena observed in toning the silver image with a platinum solution.

Free acids in the developing-bath are much less injurious, provided they do not exceed a certain limit. We make it a rule to test the developer from time to time, and, when necessary, we add oxalic acid until blue litmus paper is distinctly turned red. Instead of oxalic, citric or tartaric acid may be used; but not acetic acid, since not only is the latter

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<sup>1</sup> This reaction was even observed when not more than 8 per cent. of oxalic acid was mixed with the sensitizing solution.

<sup>2</sup> Such acids may occur in carelessly prepared chloro-platinite of potassium; this salt should, therefore, be carefully tested for a neutral reaction.

<sup>3</sup> Like nearly all the metallic salts, ferric oxalate has a distinctly acid reaction, even when no free acid is present; the condition "neutral," therefore, if taken literally, does not apply to ferric oxalate.

fugitive, but also it cannot prevent the formation of basic salts of iron.

*Reducing substances*, such as formic acid, hyposulphite, &c., in the sensitizing or developing solutions cause the reduction of ferric oxalate, and, consequently, sometimes fogging of the image.

*Oxidizing substances* may possibly convert the potassium chloro-platinite wholly or partially into insoluble potassium chloro-platinate. As the latter, when present in the paper, will, as a platinic salt, alter the character of the image (it makes it harder), oxidizing substances can often be used with advantage when this object is in view; but, of course, they must not act so energetically that the oxidation is able to take place in the sensitizing solution; the crystalline precipitate of potassium chloro-platinite which is thrown down could not by any means be made to distribute itself equally over the support of the image. We find that chlorate of potash is the oxidizing substance which gives the best results. If that salt is added to the sensitizing solution, the latter will not be decomposed; but, so soon as the solution has dried into the paper, the chlorate of potash exerts its oxidizing influence. This reaction can be explained by the fact that ferric chlorate is first formed—an exceedingly unstable body, which decomposes in drying, and then produces the oxidation of the potassium chloro-platinite. It is, however, necessary to be extremely careful in using chlorate of potash, as the presence of even one-hundredth per cent. of that substance has a noticeable effect on the image. This effect will be observed in the heightened brilliancy of the picture, which, when the proportion of chlorate is increased, may have the character of hardness. A further consideration is, that the addition of potassium chlorate will, as may naturally be conceived, lower the sensitiveness. By regulating the amount of this salt to be added to the sensitizing solution with due reference to the character of the negative to be copied, every desired effect within certain limits may be obtained.<sup>1</sup>

<sup>1</sup> In the place of potassium chloro-platinite, the corresponding salt of sodium may be used in the sensitizing solution; the chlorate of potash may then be dispensed with, and, instead thereof, sodium chloro-platinate be substituted directly for part of the platinite.



## PALLADIUM, IRIDIUM, AND GOLD.

Although from the first we did not promise ourselves any very favourable results from the use of the above-mentioned metals, particularly as their enormous cost must stand in the way of any advantage to be derived from their use, we were yet compelled to bring them into the sphere of our experiments, for the reason that they appear in Willis's specifications of patents, not only as additions to the solutions, but also as capable alone of producing a photographic image.

So far as *palladium* was concerned, since that metal possesses very similar properties to those of silver and platinum, it was to be expected that it could be used in this process as a substitute for the latter metals. Our experiments have also completely confirmed this expectation. Photographs may be taken with palladious chloride equally as well as with platinous chloride; they have a sepia-brown colour, and, on being developed, after a lengthy exposure they show the deeper shadows actually lighter than the darker half-tones, so that the picture appears to be solarized. A further peculiarity of palladium photographs is that they can be toned rapidly in a bath of gold, taking a violet colour, when the previously mentioned effect of solarization disappears.

Mixtures of the palladious and platinous chlorides have a colour which varies between brown and brownish-black, according as the quantity of the former salt prevails. This brown colour, however, as we shall show in the practical details of the process, can be obtained in a simpler and less expensive way; so that we do not recommend the employment of palladium, either alone or combined with platinum.

*Iridium*, which is also included in the platinum group of metals, behaves, in its action with reducing agents, quite differently from platinum and palladium. The properties of the compounds of iridium have considerable similarity with those of the compounds of platinum; but, on the other hand, they resemble in many points the salts of iron. These purely chemical considerations are sufficient, notwithstanding Willis's assertions, to lead us to the conclusion that the salts of iridium cannot be used in any photographic process depending

on iron.<sup>1</sup> For the reason already given, however, we endeavoured to use iridium chloride and its double salts for taking photographs, but obtained only negative results: we were unable to develop an iridium image.

As regards *Gold*, most compounds of this metal are reduced by solutions of the oxalate to metallic gold, even in the cold. On this account, the employment of gold chloride and its double salts seemed not to be feasible. One of the salts of gold, the hyposulphite, might perhaps be used with effect. This compound is not reduced by ferric oxalate in the cold; but the reaction takes place when hot solutions of potassium ferrous oxalate are employed. Our experiments, however, with this substance added to the sensitizing solution gave no results worthy of mention; so that we refrained from pursuing our investigations further in this direction.

#### ON THE RELATIVE PROPORTIONS OF PLATINUM AND IRON SALT IN THE SENSITIZING SOLUTION, AND ON THE DEGREE OF CONCENTRATION OF THE LATTER.

According to the description which we have already given of the course of the reaction in the developing solution, the quantity of ferrous oxalate theoretically necessary to reduce one gramme of potassium chloro-platinite to metallic platinum ought to be 0.69 gramme. This quantity of ferrous oxalate, which should be formed by exposure to light, would correspond to 0.9 gramme of ferric oxalate to every gramme of platinum salt in the developing solution. But, in order to

<sup>1</sup> The metals of the platinum and iron group may be arranged, according to their properties, in the following way:—

Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

An examination of this table shows us at once that Platinum (Pt) and Palladium (Pd), which approach nearly to Gold (Au) and Silver (Ag), are adapted for the production of the photographic image by means of development with the salts of iron; while the compounds of Osmium (Os), Iridium (Ir), Ruthenium (Ru), and Rhodium (Rh), which come closer to Iron (Fe), will probably not answer the purpose. It also explains the reason why palladium images, which approach closely to silver images, can be readily toned with solutions of gold, while this property is only moderately apparent in platinum images.



avoid loss of platinum, it will be always better to obtain a slight excess of ferrous oxalate,—quite apart from the doubt already expressed as to the perfect correctness of Berkeley's formula.

That, in fact, a small excess of ferric oxalate is necessary in order to obtain good results is shown by a series of experiments undertaken by us, in which we found that the ratio of platinum salt to iron salt varied from 1:0.9 to 1:1.5. Our best results were obtained with from 1.0 to 1.2 part of ferric salt to one part of platinum salt. A less or a greater proportion of ferric salt produces incomplete reduction of the platinum salt, and gives weak pictures with grey instead of black shadows. In order to explain this result in cases where a large excess of ferric oxalate is used, we can only suppose that, during the exposure necessary for producing the image, some of the ferric salt remains and settles itself in the interstices between the particles of ferrous and platinum salt, and that this remainder acts as a restrainer during the development.

The amount of platinum salt in relation to a given surface of the selected support for the image—paper, canvas, or wood—depends, in the first place, on the character of the result which it is desired to obtain. When deep blacks are required in the picture, we may estimate that for every thousand square centimetres of surface there should be from 0.02 to 0.025 gramme of potassium chloro-platinate. But it should be noted that, when the support is more porous and absorbent, the quantity of platinum salt must be increased somewhat, as, if the image has a tendency to sink into the support, part of the effect will be lost. On the other hand, when the picture is not to have any great depth, or when it is intended to retouch the image, or to paint over it (as, for instance, in the case of enlargement), the amount of platinum salt may be reduced. It is, therefore, necessary to dissolve the platinum and ferric salts in sufficient water, that the above-mentioned quantity of platinum salt may be equally distributed over the unit of surface of the support. Care must be taken that the solution is as concentrated as possible, in order to prevent it from sinking too much into the support. Further instructions on these points will be found in the practical details of the process.

## II.—PRACTICAL DETAILS OF THE PROCESS.

From the results of our experiments, as already described in the foregoing theoretical division of this treatise, we have been able to construct a method for producing platinotypes which, we believe, will be found to be easy for any one to work. The details of this method we now proceed to give at some length. The process itself naturally falls into the following operations :—(1.) Preparation of the paper, or other suitable support ; (2.) Sensitizing the same ; (3.) Copying ; (4.) Developing ; (5.) Finishing the picture.

## CHOICE AND PRELIMINARY TREATMENT OF THE PAPER.

For the purposes of the platinum process any kind of properly sized paper is suitable, provided it has an even surface, and is free from all kinds of impurity, especially from particles of metal. As a general rule, therefore, the papers specially prepared for photographic work will be found best adapted for our object, since they comply most closely with the above-named conditions. In selecting the particular kind of paper two points must be carefully attended to, namely, its strength and the nature of its surface. Ordinary photographic papers, as bought in the shops, are rather too weak to withstand the manipulations presently to be described ; they tear easily, and can therefore only be used for pictures of the smaller sizes. The stronger papers are also to be preferred to the weaker sorts for another reason—because of the greater vigour and brilliancy of the photographs taken on tough paper.

In deciding whether to use a paper with a smooth or with a rough surface, reference must be made to the nature of the picture it is required to copy. Pictures in which the finest details have to be reproduced, such as smaller portraits, should be taken on a smooth paper ; those, on the other hand, which depend for their effect on the general impression they convey, or which have to be finished and coloured in pencil or chalk, like landscapes, copies of paintings, enlargements, &c., will be best taken on rough paper. This rough



paper must have a felt-like surface, not one showing the grain, as so many drawing-papers do. Paper of this kind is seldom found in the market; it is a plain unglazed paper, which does not leave the mill in the state in which it is required for the platinum process, but only after being hot pressed.<sup>1</sup>

We ought also to warn our readers that ultramarine is used to blue many of the papers to be met with commercially, and that papers thus coloured turn yellow on being treated with hydrochloric acid. Any paper to be employed in the platinum process should therefore be tested for this pigment. It will be found that papers coloured with cobalt blue (smalt) are best suited for this purpose.

Paper which has been bought in the shops must, before being sensitised, be treated with a solution of gelatine arrow-root or algeine. This is done in order partially to close the pores of the paper, and so to prevent the sensitising solution from sinking too deeply into its substance. But the pores must not be quite stopped; otherwise the image, which consists of metallic platinum in a highly subdivided state, will be entirely on the surface of the paper, and is liable to be washed away in developing. For this reason albuminized paper, of which the film has been coagulated, or highly gelatinized paper cannot be used.

The strength of the gelatine, starch, or algeine solution, depends entirely on the kind of paper employed; paper not very strongly sized takes a concentrated solution, that more highly sized a more dilute solution, of gelatine. A couple of trials are sufficient to enable us to regulate this operation. In the papers tried by us,<sup>2</sup> whether smooth or rough, we used

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<sup>1</sup> For the information of those who wish to take up platinum-printing, we may mention that the paper used by us in our work was made expressly for us by Messrs. Gustav Röder & Co., of No. 10, Wallfischgasse, Vienna I., at their paper-mills at Marschendorf. It bears the name of "ivory vellum paper," and may be obtained either hot pressed or unglazed.

<sup>2</sup> The paper we use is half sized (resin-size). More highly sized rough paper can be treated with a from 10 to 20 per cent. solution of dextrine, instead of gelatine or arrowroot; this is passed over the surface with a sponge. Dextrine forms a temporary coating, which prevents the sensitizing solution from penetrating too deeply, but which is again removed by developing and washing, so that the paper recovers its original velvety appearance.

baths containing 1 per cent. of gelatine or arrowroot.<sup>1</sup> Gelatine paper gives a bluish-black, arrowroot paper rather a brownish-black, tone; and this difference of colour is more perceptible with smooth than with rough paper. The treatment of the papers by floating on these solutions will be an easy matter for those who are accustomed to prepare albumen or arrowroot paper; those who have had no practice in the operation of floating will have some trouble to get rid of the air-bells which, especially in the case of rough paper, adhere to the surface. For the latter, it will be perhaps easier to dip the paper in the solution, as we ourselves generally do. The following is our practice in this operation:—

#### PREPARATION OF THE SOLUTIONS.

*Gelatine.*—Ten grammes of this substance<sup>2</sup> must be allowed to soften for about half an hour in 800 c.cm. of water; the water is then poured off into a clean porcelain or perfectly enamelled iron basin, and heated therein to about 60° C. The gelatine is placed in this hot water, and, when it is dissolved, 3 grammes of alum,<sup>3</sup> and 200 c.cm. of alcohol<sup>4</sup> are added; such a solution does not set, if kept in a warm room (heated to 18° C.). It must be filtered through clean canvas into a porcelain or papier-mâché tray, which is somewhat longer than the paper on which the print is to be taken; and care must be taken that the bottom of this tray be not covered to a greater depth than 3 cm., or there will be some difficulty in dipping the paper properly into it.

*Arrowroot.*—Ten grammes of arrowroot are rubbed up in a mortar with a little water, and then poured slowly, with continuous stirring, into 800 c.cm. boiling water. After the liquid has boiled for a few moments, the vessel is taken from the fire, and to the thin paste thus formed 200 grammes of alcohol are added. The whole is then strained into a tray.

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<sup>1</sup> Paper treated with algeine behaves just the same as that treated with arrowroot.

<sup>2</sup> Any kind of good gelatine, such as is used in collotyping or emulsion-making, may be used.

<sup>3</sup> The addition of alum makes the gelatine after drying insoluble, and therefore better able to resist the hot developing solution.

<sup>4</sup> Alcohol must in every case be added to the solution to prevent the formation of air-bells, which are liable to occur in large number.



## PREPARATION OF THE PAPER.

The paper is prepared in precisely the same way, whichever of the solutions is used. The sheets are dipped, one by one, gradually into the solution, with that side downwards which is to receive the print, beginning at one of the smaller edges. After any air-bells which may adhere to the surface have been removed by means of a hair brush, the sheet is drawn out of the solution, and then dipped into it again in a reversed position. By gently shaking the tray the sheet may be kept continually submerged in the liquid. After about two or three minutes of this bath, the sheet is held by two of its corners, and drawn out with a single rapid and continuous motion; it is then fastened to a string by means of clips, or to a wooden rail by means of drawing-pins, and left hung up to dry. Air-bells which remain on the reversed side of the sheet need not be noticed; but if there are any attached to the front side, they can be removed with the tip of the finger.

Drying the paper should be effected in a warm place, and the temperature must be such that the superfluous gelatine solution may drop off, and not collect at the lower edge of the sheet to set in a ridge. As, owing to the vertical position of the sheet during drying, the part towards the lower end will contain always more gelatine than the upper, the above-described operation will have to be repeated, taking care to hang it up, after it has been gelatinized the second time, with the originally upper edge downwards.

Coating the paper can be accomplished very rapidly; if it be dried quickly (in winter near a stove, in summer exposed to the sun), the second application of gelatine can be undertaken from 15 to 20 minutes after the first. The sheets of paper, when perfectly dry, are kept ready for use, protected from dust and moisture. They will keep for any length of time, and can, therefore, be always kept in stock.

## PREPARATION OF OTHER SUPPORTS.

*Linen or other Fabrics.*—These can be treated in the same way as paper. To keep them smooth, they should be stretched on wooden frames, after the second coating with gelatine, by

means of drawing-pins. Smaller pieces, which become creased in drying, can be made smooth again by pressing between sheets of cardboard.

*Wood.*—When this substance is employed as a support, it must be in the form of plates, planed or rubbed smooth by the carpenter; these are then coated with a solution of gelatine, or a three per cent. part of arrowroot, until they no longer absorb moisture. So soon as they are dried on the surface, they can be kept ready for use between two boards, so as to prevent them from warping.

### SENSITIZING THE PAPER.

The mixture of chloro-platinite of potassium and ferric oxalate, which, as mentioned above in the theory of the process, is used for sensitizing the paper, must, on account of its great sensitiveness, only be employed under a very faint light. Lamplight, by reason of its yellow colour, is not suitable for laying on the solution: the parts that are coated cannot be distinguished from those that are untouched, and it therefore becomes difficult to avoid leaving smears and other inequalities. Perhaps the most convenient light is that at the back of a room darkened by curtains, but, even then, great care must be taken to expose the sensitized paper only in the bare time required for coating, otherwise fogging is liable to be caused. During the operation, the bulk of the sensitizing solution must be kept in the dark: sufficient to sensitize a single sheet being each time measured off and brought to the light.

### PREPARATION OF THE CHLORO-PLATINITE OF POTASSIUM.<sup>1</sup>

As only brief and scanty directions for preparing this salt are to be found in works on chemistry, we examined ourselves all the methods adapted to the purpose, and selected those which, on the one hand, worked in the simplest and

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<sup>1</sup> The preparation of chloro-platinite, as well as that of ferric oxalate, are operations which can only be properly carried on in a chemical laboratory. Those who are not chemists will do best to obtain these salts from a chemical manufactory.



most rapid manner, and, on the other hand, gave the most productive result. For our raw material we naturally took the common chloride of platinum, which can be obtained everywhere commercially.

Our objection to the method generally given for the production of the required double salt—that by means of chloro-platinite of potassium and cuprous chloride—lies in the fact that it implies, first, the formation of the double chloride and afterwards the separation of the chloro-platinite of potassium from the cupric chloride. It therefore seemed to us to be more convenient to commence with the conversion of the platinic into the platinous chloride, and then from the latter to produce chloro-platinite of potassium by adding potassic chloride. The first of these operations is best effected by reducing with sulphurous acid. With this object 50 grammes of chloride of platinum are dissolved in 100 c.cm. of water, and the solution filtered, if necessary. This solution is then heated to  $100^{\circ}$  C. in a water bath, and a strong stream of washed sulphurous acid, in the gaseous state, is passed through it. After a while the intensely yellow liquid will begin to turn red, and this is a sign that the platinum chloride has for the greater part been converted into the platinous chloride. From time to time a drop of the liquid is removed by means of a glass rod, and tested, to see whether with a solution of ammonium chloride it produces the characteristic yellow precipitate of chloro-platinate of ammonium. This test is best performed by bringing together, on a watch-glass, a drop of the solution of sal-ammoniac and one of the solution of platinum. By a comparison of the quantity of precipitate formed, it is easy in this way to regulate the process of reduction; if only a slight formation of the chloro-platinate of ammonium is observed, the stream of gas should be moderate, in order to prevent the reaction from being completed too quickly. So soon as there is no precipitate formed, and none can be produced by rubbing the watch-glass with the glass rod, the flow of gas must be at once interrupted. The conversion of the chloride is now complete, and any further flow of sulphurous acid would be injurious, since a continuation of it means loss of platinum. For, if the action of the gas be continued too long, the platinous chloride is converted into platinous sulphide—a salt which cannot be reduced by an organic ferrous salt. If, on

the other hand, the stream of gas is too soon interrupted, the liquid will still contain some platinic chloride, and this, when the solution of platinum is afterwards mixed with one of potassium chloride, will separate as insoluble chloro-platinite of potassium.

Hence the reduction of a solution of platinic chloride by means of sulphurous acid gas is an operation requiring the greatest care and attention, particularly towards the end. The solution thus obtained consists of a mixture of platinous chloride, sulphuric acid, and free hydrochloric acid. To convert it into chloro-platinite of potassium, it must be poured, when cold, into a porcelain basin, and a hot solution of 25 grammes of chloride of potassium<sup>1</sup> in 50 c.cm. of water mixed with it, stirring all the while. The chloro-platinite of potassium then separates in the form of a crystalline powder. After allowing this to cool for twenty-four hours, the crystalline precipitate is collected in a filter, and the mother-liquor is drained off; it is then washed with very little water, and afterwards with alcohol, until the latter has no longer an acid reaction.

The powder is now spread out on filtering-paper, and placed to dry in a room to which the light has no access. This precaution seems to be necessary, for the reason that a salt of platinum moistened with alcohol is very liable to become reduced if exposed to the light. The salt prepared in this way is perfectly pure, and in a state to be used for making the sensitizing fluid; any further purification by recrystallization is therefore quite unnecessary. Provided the above directions are attended to, 74 or 75 grammes of the double salt will be obtained from every 100 grammes of platinic chloride, amounting to about 93 per cent. of the quantity which should be obtained on theoretical considerations. No effort need be made to obtain from the mother-liquor a still further production of potassium chloro-platinite. The former may be worked up with the other platinum residues.

When the chloro-platinite of potassium is bought from the manufacturer, it should be tested for purity in a twofold direction :—(1) One part of the salt should be completely

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<sup>1</sup> An excess of potassium chloride is purposely used, in order to effect the complete separation of the double salt.



soluble in about six parts of cold water; and (2) the solution thus obtained must not possess an acid reaction. Both the salt and its solution resist perfectly the action of light and of the atmosphere, and no special precautions are therefore requisite in preserving them. For the production of platino-types, a solution is prepared of 1 part of the salt in six parts of distilled water, and this can always be kept in stock. We shall call this the normal solution of platinum.

#### PREPARATION OF THE FERRIC-OXALATE SOLUTION.

For the preparation of this solution of ferric-oxalate the following operations are necessary:—(1) Manufacturing the ferric hydrate; (2) dissolving that substance in oxalic acid; (3) determining the amount of iron and of oxalic acid contained in this solution; (4) diluting and acidulating the same.

The method of preparing ferric hydrate is generally well known, but for the sake of completeness we will give a brief description of it. Ferric chloride, 500 grammes, are dissolved in from five to six litres of water, and, when the solution has been brought to the boiling point, solution of soda is added until it gives with litmus paper a distinctly alkaline reaction. For this purpose about 250 grammes of caustic soda will be found necessary. The precipitate is then washed with hot water by decantation, until the wash-water is no longer alkaline. It is next placed in a cloth, and by pressure freed from the greater part of the water. With the ferric hydrate thus obtained, which ought to have a syrupy consistency, there should be mixed about 200 grammes of finely crystallized oxalic acid, and the mixture be then left to itself for a few days at a temperature of not more than  $30^{\circ}$  C., and in a place completely protected from the light; under these circumstances the formation of ferric oxalate will go on steadily. Some persons recommend the promotion of this process by digesting the mixture for some time at a high temperature; this we are decidedly opposed to, since, by heating for even a few hours to  $50^{\circ}$  or  $60^{\circ}$  C., the salt will be partially reduced to ferrous oxalate. At the commencement the solution has a pure green colour; by continued digestion it turns yellowish-green, and finally greenish-brown. When this moment has arrived the remaining ferric hydrate should be

filtered off, and the solution be submitted to a quantitative chemical analysis.<sup>1</sup>

Although the determination of the amount of iron and oxalic acid contained in the solution is one of the simplest of analytical operations, we tried at first to dispense with it. Closer investigation, however, proved to us how necessary it is to confine the relations between rather narrow limits, in order to ensure the success of the platino-ferric process. Now as ferric oxalate cannot be prepared in a stable form, so as to have a constant composition, there remains no other way than that of determining the composition of the solution by analysis and then diluting it to the required degree. Further it should be noted that any quantity of the solution may be prepared at once, and then kept in stock.

From the analysis we ascertain the quantity of ferric oxalate contained in 100 c.cm. of the solution, as well as any slight excess of oxalic acid which happens to be present. The liquid is then diluted with so much distilled water, that every 100 c.cm. of it may contain 20 grammes of ferric oxalate  $[\text{Fe}_2(\text{C}_2\text{O}_4)_3]$ . Crystallized oxalic acid is then added, until, with the free acid already in the mixture, that substance amounts to from 6 to 8 per cent. of the ferric oxalate already in the solution—the normal ferric solution.

An iron solution purchased from the chemist must be tested in the following manner before it is used :—It must not turn blue with a solution of ferricyanide of potassium (red prussiate of potash). When boiled and diluted with ten times its quantity of water, it must not become turbid. From the first reaction we ascertain the absence of ferrous salts ; from the second, that of basic ferric oxalate.

In order to introduce into the sensitizing solution some chlorate of potash, which in certain circumstances is necessary, the best way is to keep ready for use a mixture of chlorate and

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<sup>1</sup> To perform this analysis a few c. centimètres of the solution are measured off, and the oxalic acid then determined from measure by means of permanganate of potash ; the amount of iron in the same liquid may be ascertained in the same way, after reduction by means of zinc. But it is perhaps more convenient to determine by weight the iron in a separate portion of the solution ; this can be done by evaporating, heating to redness, incinerating with nitrate of ammonia, and weighing the ferric oxide which remains.



ferric solutions. It can be prepared by measuring off a certain quantity of the normal ferric solution, and mixing with it so much chlorate of potash as to cause 100 c.cm. of the liquid to contain 0.4 gramme of the salt. This is the normal chlorate of iron solution.

Both the ferric solutions must be kept away from the light.

#### PREPARATION OF THE SENSITIZING SOLUTION.

The sensitizing liquid is prepared by mixing portions of the platinum and iron solutions and afterwards diluting with water. In the normal sensitizing solution we give the following prescription :—

24 c.cm. of platinum solution,  
22 „ „ ferric solution,  
4 „ „ water.<sup>1</sup>

This works very soft, with deep blacks.

In order to produce rather more brilliancy, the following composition may be used :—

24 c.cm. of platinum solution,  
18 „ „ ferric solution,  
4 „ „ ferric-chlorate solution,  
4 „ „ water.

To obtain results corresponding to silver images mix—

24 c.cm. of platinum solution,  
14 „ „ ferric solution,  
8 „ „ ferric-chlorate solution,  
4 „ „ water.

For very weak negatives, reproductions, engravings, &c.—

24 c.cm. of platinum solution,  
22 „ „ ferric-chlorate solution,  
4 „ „ water.

When the pictures have no perfectly black shadows, as in the reproduction of pencil drawings, the mixtures, as given above, may be diluted with half or equal volumes of water. If the solutions are to be applied to surfaces with but little

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<sup>1</sup> Distilled water must always be used for diluting. Ordinary spring water contains lime, and produces turbidity owing to the formation of calcium oxalate.

absorbing power, *e.g.*, highly sized and hot-pressed paper, the addition of water to the mixtures may be altogether omitted.

### COATING THE PAPER.

Immediately before using, one of the mixtures recommended above should be prepared by measure in a measuring-glass,<sup>1</sup> in quantity corresponding to the size of the sheet to be sensitized. While it is being coated, it will be best to keep the paper stretched, by means of clips, on a strong plate of glass which is only a little larger in dimension than the sheet itself. For this purpose we adopt the following simple arrangement.

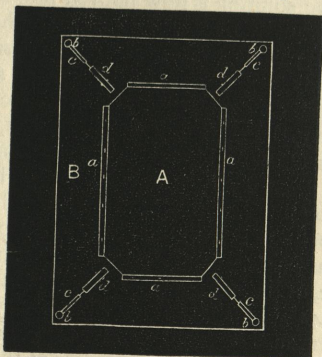


FIG. 1.

In Fig. 1, A is the glass plate (a copying-frame plate), whose corners have been cut off obliquely for about  $1\frac{1}{2}$  or 2 centim. It is kept fixed immovably on the top of a table, or on the surface of a plane drawing-board, B, by means of the little wooden ledges, *a, a, a, a*. At the corners of the board are screwed on small hooks, *b, b, b, b*, to which, by means of elastic threads, *c, c, c, c*, are attached the wooden clips, *d, d, d, d*.

<sup>1</sup> For the particular kind of paper which we had selected (the size of the sheet is  $50 \times 66$  centim. = 3,300 sq. centim.), we used 10 cub. centim. of one of the above-mentioned aqueous solutions per sheet. This is according to the proportion of platinum and ferric salt per unit (1,000 sq. centim.) of surface, as obtained on theoretical considerations.



The sheet of paper to be sensitized is laid on the plate A, and kept stretched by the clips which seize the corners of the paper where they project over the edges of the glass. By means of this arrangement the paper remains stretched during the process of coating, since as fast as it expands, through absorption of the sensitizing liquid, the elastic threads contract and draw the clips outwards. When a smaller sheet is to be coated, or when an experiment merely is being tried, it will be sufficient to stretch the paper to be sensitized on a clean plane drawing-board by means of a couple of drawing-pins, taking care, however, to prevent the sensitizing liquid from coming in contact with these latter, or it will be contaminated.

The platino-ferric solution is now poured into a shallow basin, and then spread equally over the surface of the paper with a flannel pad. The pad is drawn, without pressing,<sup>1</sup> in every direction backwards and forwards, until the sheet is everywhere equally moist, and appears to be quite free from streaks. Instead of the flannel pad, a soft bristle brush, mounted on a wooden handle, may be used with effect for applying the solution, and it may then be distributed equally by means of a round brush, also mounted in wood. When the sheet is sensitized, it must be hung up, by means of clips or drawing-pins, in a dark room, and so soon as the moisture has disappeared from the surface, it is left to dry quickly at a moderate temperature (30° to 40° C.) near a stove or in a drying-oven.

Great attention must be paid to the operation of drying, as an error therein may jeopardise the success of the whole process. If the paper is placed too soon to dry in the warmth, the sensitizing liquid will remain too much on the surface of the paper, and the image is liable to come off in developing. On the other hand, if the paper is left too long before being hot-dried, the sensitizing liquid sinks too deeply into the substance of the paper, and the print will be weak, without soft blacks. As a rule, the operation of drying, reckoning from the time when the coating is completed, should not extend over a longer period than ten minutes. In the rapid desiccation, the limits of temperature above given should not be exceeded, otherwise

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<sup>1</sup> Any strong rubbing with the pad, particularly when the paper is rough, may affect the homogeneity of the film, and the picture when finished has a grainy appearance in the half-tones.

partial reduction of the salt of iron may take place, even though protected from the action of light.

The flannel pad should be changed every quarter of an hour. As the paper is coated with the sensitizing solution by weak daylight, and the pad is therefore exposed to light to a certain extent during the operation, the ferric oxalate absorbed by it is reduced, though the reduction may only be very slight. It should also be remembered that the sensitizing solution, when once mixed, will gradually decompose, even though kept carefully in the dark. Hence, with continuous use of the same pad, some of the ferrous oxalate would be left on the paper, and produce spots and streaks on the picture after development. When a brush is used to apply the sensitizer, it should be washed from time to time in clean water. For the reason above given, the sensitizing solution should be all used up as soon as possible, and it is also distinctly necessary to mix only so much of the solution as will be directly required.

When thoroughly dry, the sheets of sensitive paper, as well as the finished copies, are kept in chloride of calcium boxes. The construction of a box of this kind is shown in the cuts below (Figs. 2 and 3). A is the space in which the papers are

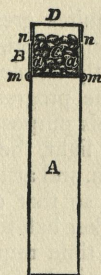


FIG. 2.

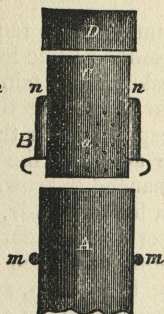


FIG. 3.

kept. The cover B is divided into two parts: the lower part, C, which is placed on the top of the box, consists of a cylinder, *a*, perforated with holes, like a sieve, sliding into the box A, and contains some lumps of perfectly dry chloride of calcium,



wrapped in a piece of swansdown calico. The upper part D fits on to and closes the top of the cylinder, *a*. In damp localities it will be well to keep the slots, *m, m*, air-tight by slipping over them an elastic ring. From time to time the calcium chloride should be examined to see that it is perfectly dry. If it is observed to be at all moist, it must be changed for a fresh and dry supply. Damp calcium chloride can readily be deprived of its moisture by heating in an iron vessel, and so rendering it again fit for use.

An indispensable condition of obtaining good prints is the absolute dryness of the paper, both before and after copying. Moist paper will give, probably in consequence of more or less reduction of the ferric salt, weak and foggy images; moreover, its sensitiveness is less. For this reason it is advisable to place a piece of waterproof cloth in the printing-frame behind the sensitized paper, and this will protect the paper from any atmospheric influence while it is being printed. In damp weather it may be necessary to warm and dry the pad of the printing-frame before arranging the latter.

### PRINTING THE PICTURE.

Printing in platinum-printing requires greater care than in silver-printing, because the actinic impression, although distinct, is, comparatively speaking, only faintly visible. It is necessary to get accustomed to controlling the progress of the printing-operation; but the experience for this purpose is acquired after a few trials. By the action of the light, the yellow colour of the paper becomes changed to brown, and after longer exposure this again turns of a lighter shade, so that often the deepest shadows appear lighter than the darker half-tones.

Accurate instructions as to the time required for printing can, of course, not be here given, as it depends entirely on the density of the negative and on the conditions of light prevailing at the moment. We can, however, state with certainty that platinum paper is at least three times as sensitive as silver paper, and that this greater sensitiveness makes itself more felt in dull than in bright weather. This is owing to the greater sensitiveness of ferric oxalate to the less refrangible rays of the spectrum. For a good portrait negative of average intensity, we gave from

twenty to twenty-five minutes with a clear sky in April ; with a thinner negative we printed for fifteen minutes. When the prints have been taken, and it is not desired to develop them at once, they are kept, as already described, in a chloride of calcium box.

### DEVELOPING THE PICTURE.

To develop the picture we take a saturated (in the cold) solution of potassium-oxalate,<sup>1</sup> acidulated with oxalic acid.<sup>2</sup> For heating the solution we may employ either a glass boiling-flask or a vessel of enamelled iron ; but this supposes that only a small number of pictures of moderate size are to be developed in a basin by pouring the solution over them. When they are of large size and in greater number this method would not answer, as the solution cools by being poured over the picture, and therefore will have to be heated afresh.

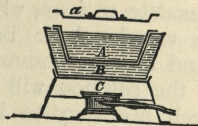


FIG. 4.

In this case we prefer to use a vessel of flat or bent enamelled iron of the same width as the picture, which can be placed over a water bath. The section of a developing-tray of this kind is shown in Fig. 4 ; A is the enamelled iron vessel, containing the oxalate solution, *a* its cover of zinc plate ; B is another hollow vessel, with double wall of zinc plate, which acts as the water bath ; C is a gas or spirit lamp. The vessel B is filled with hot water through a tube let into the upper side, and the hot solution of oxalate is then poured into the tray A ; it can readily be kept at the required temperature by means of the lamp underneath. To develop it, each print is taken separately

<sup>1</sup> For other good developing solutions, see Part II, "The Theory of the Process."

<sup>2</sup> In Part II it is explained why the solution of potassium-oxalate must have an acid reaction.



by two opposite sides and drawn slowly through the solution.<sup>1</sup> Development takes place at once, the brown colour changing immediately to a deep black.

If, by chance, any part of the picture does not come in contact with the solution, as, for instance, where any air-bells adhere to it, it must be again drawn through the solution. When there is danger of the print having been too long copied, a somewhat cooler solution of potassium-oxalate may be used, though the hot solution always works best. The temperature of 80° C., as given above, may be exceeded when the print has been copied for too short a time; we have ourselves very often employed a developing solution in a boiling state.

Finally, we would again direct the attention of our readers to the remarks in Part II, "The Theory of the Process," on the necessity of having always an acid reaction in the developer. When the solution is kept continuously at a high temperature, it may happen that the evaporation will cause crystals of potassium-oxalate to form, which will be deposited on the sides of the vessel; those being over-heated will partially decompose and form potassium-carbonate, so that in certain circumstances the solution will become alkaline. It is therefore imperatively necessary to keep testing the liquid from time to time with litmus paper, and, if necessary, to acidulate the developer with oxalic acid.

After being used, the developing solution may be poured back into a flask, and can be employed again. The water which has evaporated should occasionally be replaced, and, as often as necessary, fresh potassium-oxalate should be added.

### FINISHING THE PICTURE.

Directly the picture is developed it must be immersed in a solution of

Hydrochloric acid	...	...	...	1 part,
Water...	...	...	...	80 parts,

and left there until any of the iron-salt still present has been removed. This solution of hydrochloric acid must be changed

<sup>1</sup> To prevent the hands from coming into contact with the liquid, it is advisable to hold the print with a forceps made of bone or horn.

(twice or three times) until it no longer turns yellow. We ourselves generally change the solution three times, and leave the print in it each time for about ten minutes.

Finally, the print should be laid for a short time in a pan of water in order to remove the hydrochloric acid: ten to fifteen minutes will suffice for this purpose. Should any hydrochloric acid remain in the paper, it would not have any bad effect on the print itself, but might injure the substance of the paper, so that in the course of time it would be destroyed. To be perfectly easy on this point, it may be advisable to try the last wash-water with litmus paper, whether it comes off quite neutral.

After washing, the picture is dried in the ordinary way, and can then, if desired, be mounted on cardboard. Prints on smooth paper may be hot-pressed, to give them a slight sheen, which brings up the deep parts.

Prints on wood or linen are treated just the same as those on paper. As the plates of wood are very liable to warp, through being moistened with the sensitizing solution and then heated to dry, they should be fastened by small points or drawing-pins flat on a strong board. Linen can be kept stretched on wooden frames after being coated with the sensitiser.

At this point we ought further to point out that platinum prints in a wet state appear always more brilliant and lighter than they do when dry. A print, therefore, which while still wet after development seems to be quite right as regards tone, would be too dark when dried.

### RETOUCHING PLATINUM PRINTS.

As the prints have a smooth horny surface like albumen pictures, they lend themselves admirably to retouching, either with colour or chalk, and may even be painted or drawn upon all over. Their permanence and the absence of any substance in the film which can affect the applied colouring material protect them from the defect which in silver prints always presents itself after a time,—that is, the parts which have been painted or drawn over are observed to vary very disagreeably in colour-tone from the copy. Many sorts permit any kind of retouching; others again, as, for instance, those which are not properly sized, become disintegrated, and fall to pieces when



treated with a hot solution of ferric oxalate and dilute sulphuric acid. Such papers as these should, after being washed, be dipped for several minutes in a saturated solution of alum; they should then be dried, either with or without previous washing.

### DEFECTS, THEIR CAUSE AND REMEDY.

1. The pictures are vigorous, but more or less fogged.

- a. *Cause*.—The paper was affected by light, either in sensitizing or printing.

To prevent it, sensitize only under a weak light, and dry either in complete darkness or by lamplight.

When examining the course of the copying operation, be careful to avoid too strong a light in arranging the frame.

- b. *Cause*.—Too high a temperature in drying.

It should not exceed  $40^{\circ}$  C.

- c. *Cause*.—Spoiled ferric solution.

The ferric solution is best preserved from the influence of light by being kept in a hyalite flask. If you are not confident as to your solution, you must assure yourself, before using it, by testing with red prussiate of potash, that it is free from ferrous salt. Should it contain only a trace of ferrous salt, it can be made fit for use again by carefully adding red prussiate of potash. In order to try this, mix a few cub. centims. of the normal ferric-chlorate solution with every 100 cub. centims. of the iron solution, and ascertain, by actual experiment on paper, whether the restoration is complete.

- d. *Cause*.—Too long exposure in the copying-frame.

The time of copying should be shortened, and, if the picture is not yet developed, use a cold developer.

2. The prints appear weak under the developer.

- a. *Cause*.—Paper which has become damp.

The paper should always be kept in the chloride of calcium box, even after being printed, if not immediately developed. Paper once spoiled cannot be made good again.

- b. Cause.*—The paper is too old.

Paper can generally be kept in good condition for at least six or eight weeks, and sometimes even more ; but after that time a gradual change appears to take place, even though it be kept in the dark, and not only weak, but also fogged, pictures are the result. As neither time nor trouble are required for sensitizing the paper, we recommend only to make at once as much as may be necessary for use during three or four weeks.

- c. Cause.*—Weak negatives.

Use more chlorate of potash in the sensitizing solution.

3. The prints come out vigorous in developing, but become weak after being dried.

- a. Cause.*—Paper not sufficiently sized, for which reason the images sink into its substance.

When this is the case, employ stronger solutions of gelatine or arrowroot.

- b. Cause.*—Drying has been too slow.

The drying process should not take longer than ten minutes ; if this is exceeded, the sensitizing solution sinks too deeply into the paper.

4. The whites of the print have, after drying, a more or less yellowish tinge.

- a. Cause.*—The sensitizing solution in the developer is not sufficiently acid.

Attention should be paid to the instructions on this point in the previous divisions of the subject.

- b. Cause.*—Insufficient immersion in hydrochloric acid.

The solution of hydrochloric acid must be changed two or three times until the last change no longer turns yellow at the end of ten minutes.

- c. Cause.* Paper blued with ultramarine, which when treated with hydrochloric acid turns yellow.

Before using the paper, you must be certain that its colour does not suffer from contact with a hot solution of oxalate and from treatment with hydrochloric acid.

5. The prints come out hard.

- a. Cause.*—Exposure too short.

- b. Cause.*—Too much chlorate in the sensitizing solution  
The remedy for this defect stands to reason.



## 6. Spots and streaks.

*Causes.*—Dirty brushes; touching the paper with wet fingers; dirty glass plates, vessels not kept clean, &c.

## 7. Black spots.

*a. Causes.*—Particles of metal imbedded in the substance of the paper, causing a reduction of the platinum.

*b. Causes.*—May be due also to insoluble impurities in the chloro-platinite of potassium. These spots have a black nucleus, with an extension, like the tail of a comet, of lighter colour.

In such a case, filter the sensitizing solution.

## USING UP THE PLATINUM RESIDUES.

Considering the high price of platinum, it will reward the operator carefully to collect all the waste and residues from this process, and to convert them again into the metal or the chloride of the metal.

1. *Using up old Developers.*—With proper treatment, we can work with the same developing solution for a considerable time; only when it becomes overloaded with salts of iron to such an extent that crystals separate, or that the colour of the liquid begins to turn dark yellow, will it be advisable to have recourse to a fresh developing solution.

Old solutions of this kind are best used up in the following way. The solution is mixed with about one-fourth its volume of a saturated solution of ferrous sulphate and heated to boiling point in a porcelain basin. Platinum then separates in the metallic state, and can be collected on a filter. The filtrate is a solution of ferrous oxalate, and can, in the same way as the old iron developer of the negative process, be converted into potassium oxalate.

2. *Using up waste Platinum-paper, spoiled Prints, &c.*—The whole of the paper, linen, flannel, &c., containing any salt of platinum or metallic platinum, is collected, and, when a considerable quantity has been brought together, it is incinerated. The ashes remaining after the incineration are stirred up into a thin paste with a mixture of three parts concentrated hydrochloric acid and one part nitric acid; this is then set to digest for a few hours at a temperature of from 50° to 70° C. After this, it is diluted with an equal quantity of water, then filtered, and the

insoluble remainder washed in the filter with water. From the filtrate and wash-water the platinum is precipitated by adding ammonia, as chloro-platinate of ammonium, and this being heated to redness is then converted into metallic platinum.

3. *Residues of the sensitizing Solution.*—Any other liquids containing platinum may be mixed with the filtrate obtained by the method described under (2); they can then be worked up together. The metallic platinum obtained by (1) and (2) must be digested in hot hydrochloric acid, to get rid of any remaining trace of iron, and then converted by the well-known method into platinum-chloride by means of *aqua regia*.

#### VALUE OF THE PLATINOTYPE PROCESS.

The chief advantages of this process are (1) the simple nature of the manipulation, which can be carried out much more plainly and readily than in any other printing process; (2) the great sensitiveness, to which attention has been already drawn; (3) the perfect permanence of the prints; (4) the peculiar character of the pictures, which, from an art point of view, give them a much higher value than belongs to silver prints. Owing to the exceeding sensitiveness of the platinum process, from three to four times as many prints may be taken in the same time as is possible with the silver process. This advantage should, as we have already pointed out in the Introduction, be appreciated in dull weather, more especially in winter-time, when printing by the silver process is nearly impossible.

After being printed, the pictures can be completely finished in half an hour, and are then ready to be mounted. All the wearisome washing, toning, fixing, and again washing, which are necessary for silver prints, are dispensed with in the platinum process, and the great care which must be taken to obtain good results by the former is quite unnecessary in the latter process. Only very careless treatment causes the picture to be spoiled. For producing platinum prints only one operation—that of sensitizing—requires any degree of attention; while, for silver prints, time, trouble, and care must all be given to obtain pictures which, after all, are only of doubtful permanence. When we take into consideration also that if silver prints are not washed with extreme care and attention they, in



a short time, are quite spoiled, while a mistake in the same direction with platinotypes is of no importance, we cannot fail to see the great advantage which platinum prints possess over those in silver.

Even most carefully prepared silver prints fade in the course of time, owing to the finely divided silver and gold not being able to resist for any length of time the influences to which even under the most favourable circumstances they must be submitted. Now, in the platinotype the image consists of platinum—metal which can be attacked by scarcely any known reagents. There can, therefore, be no doubt that such an image may be regarded as completely unchangeable. According to our own experiments repeatedly made, the image is quite unaltered after being submitted for hours to the action of hydrochloric acid, mixtures of hydrochloric and sulphuric acids, even of solution of calcium chloride; only *aqua regia* was able to affect it, and then the paper itself was also destroyed; while nitric and sulphuric acids, ammonia, caustic potash, and potassium cyanide were equally without effect.

We have been greatly puzzled by the statement of Van Monckhoven<sup>1</sup> that platinum images are quite as liable to fade as those of gold; according to his view, platinum is attacked by the compounds of sulphur and of chlorine which are found in the atmosphere. This opinion appears to us, to say the least, a rash one, for there can be no doubt that platinum has a far greater power of resisting chemical action than gold. Gold<sup>2</sup> is acted on by gaseous chlorine, as well as by liquids containing bromine and iodine; it is even dissolved by aqueous solutions of sodium chloride, potassium nitrate, alum, &c., while platinum is not affected by anhydrous liquid chlorine, and even a stream of chlorine gas at so high a temperature as 200° C. produces scarcely any effect on spongy platinum. From this remarkable power of resistance of metallic platinum even in a finely divided state, it may be concluded that a platinotype will never be affected by any traces of sodium chloride or of sulphur-compounds which may be present in the atmosphere.

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<sup>1</sup> "Bulletin de l'Association Belge de Photographie," vol. vi, p. 335.

<sup>2</sup> Gmelin's "Handbook of Inorganic Chemistry," vol. iii, pp. 1007 and 1068.

When the paper is prepared with gelatine the tone of the platinum print is a pure black ; when arrowroot is employed, a sepia-brown ; the deep shadows are velvety, the modelling tender, and the high lights a pure white. Rough paper is free from glitter, and gives the pictures the appearance of etchings ; smooth paper, when hot-pressed, has a dull sheen, which makes the details of the picture come out clearer. The great depth of the shadows is characteristic of platinum prints, and this cannot be obtained in silver prints without employing a brilliant coating of albumen.

Our opinion is that the process will become very popular, but that it will probably not supersede that of silver printing. In the latter process, on the one hand, the operation of copying is more easily regulated ; on the other, the public is too much accustomed to the brilliancy and colour of the silver prints. But for certain purposes, for instance for enlargements, reproduction, and copies from landscape negatives, the platinum process will, we believe, have the decided preference. Especially for amateurs this process offers advantages which cannot be overrated, on account of the simple nature and rapidity of the operations, and particularly on account of the small number of instruments and apparatus necessary for working it.

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The first of these is the fact that the United States is a young nation, and that its history is a history of growth and development. The second is the fact that the United States is a nation of immigrants, and that its history is a history of the struggle for a better life. The third is the fact that the United States is a nation of free men, and that its history is a history of the struggle for freedom.

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